Topics:

1) **Reaction Rates** (The change in the concentration of substance per unit time)
   a) Determine the average rate of a reaction based on the change in conc. of a substance. \( \text{Rate}_A = \frac{\Delta[A]}{\Delta t} \)
   b) Use stoichiometry to convert from the average rate of appearance/disappearance of one substance in a reaction to the average rate of appearance/disappearance of another substance in the reaction.
   c) The instantaneous rate of disappearance of a reactant is faster in the beginning of a reaction.

2) **Rate Laws**: For the reaction \( A + B \rightarrow C \) the general rate law is \( \text{Rate} = k[A]^a[B]^b \)
   a) Use experimental data of concentrations and rates to determine the order with respect to any reactant.
      - zero order—the rate does not change with change in concentration of substance.
      - first order—the rate doubles when the concentration of substance doubles
      - second order—the rate quadruples when the concentration of the substance doubles.
   b) Analyze graphs of Rate vs \([A]_0\) to determine the order of that substance. See graph→

3) **Integrated Rate Laws**: (Rate Laws consisting of concentration, \( k \) and time)
   a) Zero order: \([A]_t - [A]_0 = -kt\)  
      Graph: \([A] \text{ vs time}\) is linear  
      won’t need half-life eq.
   b) First order: \(\ln[A]_t - \ln[A]_0 = -kt\)  
      Graph: \(\ln[A] \text{ vs time}\) is linear  
      \(\text{Half-life} = t_{1/2} = \frac{0.693}{k}\)
   c) Second order: \(\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt\)  
      Graph of \(\frac{1}{[A]} \text{ vs. time}\) is linear  
      won’t need half-life eq

4) Activation Energy, Collision Theory and the Arrhenius Equation
   a) Use collision theory to explain why the rate of a reaction increases when one increases concentration of a reactant, increases surface area, increases temperature or uses a catalyst.
   b) Label energy diagrams: activation energy, activated complex, and \(\Delta H\)
   c) Use Arrhenius equation to determine how temperature and \(E_A\) affects \(k\) (rate constant)
      When \(T\) increases, \(k\) increases (rate also increases); When \(E_A\) is larger, \(k\) is lower (rate is also slower)
      \[ \ln k = -\left(\frac{E_A}{R}\right) \left(\frac{1}{T}\right) + \ln A \]  
      Graph: \(\ln k\) versus \(1/T\) is linear where \(m = -\left(\frac{E_A}{R}\right)\)
   d) Compare and calculate rate constant \((k)\) values at different temperatures →
      \[ \frac{k_2}{k_1} = \frac{E_A}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \]

5) **Reaction Mechanisms**: (Rates of reactions can be used as evidence to support a reaction mechanism.)
   a) The rate determining step is the step in the mechanism with the highest activation energy. (slowest)
   b) The coefficients of the reactants in the rate determining step are the exponents in the rate law.
      - If \( aA + bB \rightarrow cC \) is the rate determining step then the rate law is \( \text{Rate} = k[A]^a[B]^b \)
      - This is because the rate of a rxn is dependent on the molecules colliding in the rate determining step.
      - If a reactant is not involved in the rate determining step, the rxn is zero order w/ respect to that reactant.

6) **Catalysts**: chemical substances that speed up the rate of a reaction without being consumed.
   - Catalysts allow the reaction to proceed by a pathway (mechanism) that is more kinetically favorable, so the overall rate increases.
   - Catalysts often lower the activation energy of the reaction and can also increase the frequency of collision.
   - Catalysts are not consumed because they react and then they are regenerated.
Summary of formulas and plots in Kinetics Unit

<table>
<thead>
<tr>
<th>Differential rate law</th>
<th>Zeroth Order</th>
<th>First Order</th>
<th>Second Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate $= -\frac{\Delta [A]}{\Delta t} = k$</td>
<td>Rate $= -\frac{\Delta [A]}{\Delta t} = k[A]$</td>
<td>Rate $= -\frac{\Delta [A]}{\Delta t} = k[A]^2$</td>
<td></td>
</tr>
</tbody>
</table>

Concentration vs. time

<table>
<thead>
<tr>
<th>Zeroth Order</th>
<th>First Order</th>
<th>Second Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A] = [A]₀ − kt</td>
<td>[A] = [A]₀e⁻kt or $\ln[A] = \ln[A]₀ − kt$</td>
<td>$\frac{1}{[A]} = \frac{1}{[A]₀} + kt$</td>
</tr>
</tbody>
</table>

Straight-line plot to determine rate constant

<table>
<thead>
<tr>
<th>Zeroth Order</th>
<th>First Order</th>
<th>Second Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope $= -k$</td>
<td>Slope $= -k$</td>
<td>Slope $= k$</td>
</tr>
</tbody>
</table>

Relative rate vs. concentration

<table>
<thead>
<tr>
<th>[A], M</th>
<th>Rate, M/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 1</td>
<td>1, 1</td>
</tr>
<tr>
<td>2, 1</td>
<td>2, 2</td>
</tr>
<tr>
<td>3, 1</td>
<td>3, 3</td>
</tr>
</tbody>
</table>

Half-life

$t_{1/2} = \frac{0.693}{k}$

Units of $k$, rate constant

| M/s | 1/s | $M^{-1} \cdot s^{-1}$ |

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Initial Rate vs. Initial Concentration of a reactant.

- 0\textsuperscript{th} order: initial rate is the same no matter what the initial concentration of reactant.
- 1\textsuperscript{st} order: As the initial concentration of a reactant increases, the initial rate increases proportionately.
- 2\textsuperscript{nd} order: As the initial concentration of reactant increases, the initial rate increases exponentially.